

dioxide oxidation of the corresponding methyl ketones⁵ was the new compound *p*-fluorophenylglyoxal hydrate, white crystals, decomposing at 93–94°.

Anal. Calcd. for C₈H₇FO₃: C, 56.65; H, 4.13. Found: C, 56.80; H, 4.57.

We are indebted to Dr. M. J. Shear and Dr. J. L. Hartwell of the National Cancer Institute, and Dr. Louis H. Goodson of Midwest Research Institute, and their associates for suggestions and for arranging screening tests.

(5) A. H. Blatt, "Organic Syntheses," Coll. Vol. II, John Wiley and Sons, Inc., New York, N. Y., 1943, p. 509.

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The Steric Configuration of Brominated 3-Ketosteroids¹

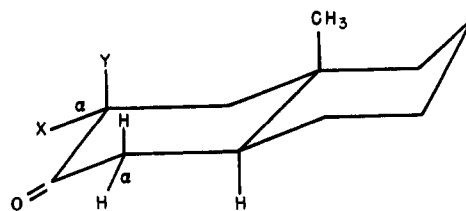
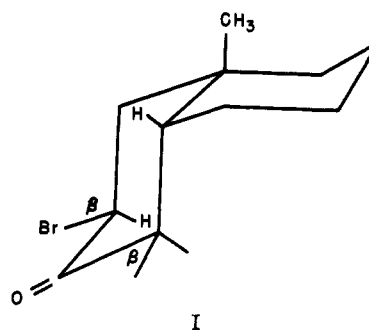
BY R. NORMAN JONES

RECEIVED APRIL 23, 1953

To explain the effects of vicinal bromination on the C=O stretching band in the infrared spectra of ketosteroids, it was postulated² that when the C—Br and C=O bonds are coplanar the frequency of the carbonyl band is increased by 15–20 cm.⁻¹, but when the C—Br and C=O bonds are perpendicular, bromination does not change the frequency of this band. This observation was subsequently confirmed by Corey who has generalized it to other cyclic α -haloketones.³

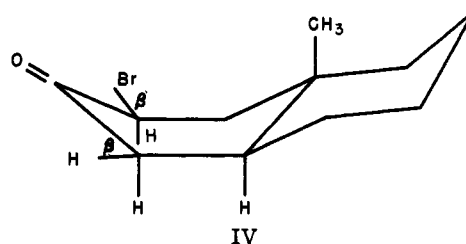
For the chair conformations I and II conventionally assigned to the A rings of normal and allo-3-ketosteroids, a positive frequency shift should occur on bromination at the equatorial C₂- and C₄-positions, and on this basis the configurations 4 β -bromocoprostan-3-one and 2 α -bromocholestan-3-one were predicted.² The 4 β -bromocoprostan-3-one structure has been substantiated by Fieser and Dominguez⁴ on the basis of chemical evidence. These investigators assigned a 2 β -configuration to 2-bromocholestan-3-one, but Fieser and Wei-Yuan Huang⁵ now regard this compound as 2 α -bromocholestan-3-one, in accord with spectrographic considerations.

The validity of the general assumption of a chair conformation for ring A in allo-steroids has been questioned by Fieser and Dominguez.⁴ In assigning the bromine configurations spectrographically this assumption was specifically made and it is the object of this note to draw attention to the fact that if 2 β -bromo-3-ketosteroids have a boat conformation IV the C—Br bond will be coplanar with the C=O bond and the conditions for a positive carbonyl frequency shift will be satisfied. It is therefore to be anticipated that the position of the C=O stretching band will fail to distinguish between 2 α -bromocholestan-3-one in the conven-



II X = Br Y = H
III X = H Y = Br

tional chair configuration, and 2 β -bromocholestan-3-one in the boat configuration IV.



There can be little doubt that the non-halogenated 3-ketoallosteroids will possess the stabler chair structure, but in the 2 β - and 4 β -bromo derivatives the bromine atoms approach closely to the C₁₀ angular methyl group in the chair form and repulsion between these groups may be sufficient to stabilize the boat structure.

Although at present it is not possible to differentiate between boat and chair conformations of ring A by infrared spectroscopy, the carbonyl absorption strongly suggests that these vicinal bromo-ketones must exist predominantly or exclusively in one conformation only. A labile equilibrium of the type III \rightleftharpoons IV should reveal itself by a broadening, asymmetry or doubling of the carbonyl band. Although such an effect has been looked for it has not been observed.

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Platinum-Olefin Compounds

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RECEIVED APRIL 3, 1953

Chatt¹ and Chatt and Wilkins² reviewed the various structures which have been proposed for olefin coordination compounds and reasons for rejecting each of these were presented. The ob-

(1) Published as Contribution No. 3060 from the Laboratories of The National Research Council of Canada.

(2) R. N. Jones, D. A. Ramsay, F. Herling and K. Dobriner, *THIS JOURNAL*, **74**, 2828 (1952).

(3) E. J. Corey, *ibid.*, **75**, 2301 (1953).

(4) L. F. Fieser and X. A. Dominguez, *ibid.*, **75**, 1704 (1953).

(5) L. F. Fieser and Wei-Yuan Huang, *ibid.*, **75**, 4837 (1953).

(1) J. Chatt, *J. Chem. Soc.*, 3340 (1949).

(2) J. Chatt and R. G. Wilkins, *Nature*, **165**, 859 (1950).